The Peroxide-Catalyzed Addition of Carbon Tetrachloride to β-Pinene[1]

BY DOROTHY M. OLDROYD, G. S. FISHER AND L. A. GOLDBLATT

The peroxide-catalyzed addition of carbon tetrachloride to olefins has been reported by Kharasch and his co-workers.[2] They reported good yields of a one-to-one addition product of carbon tetrachloride with 1-octene and lesser yields with ethylene and propylene. Biallyl was reported to give major proportions of polymeric material and styrene gave almost exclusively a polymeric addition product.

It was of interest to us to study the applicability of this reaction to terpenes obtainable from turpentine. Reaction with β-pinene (nopinene) which contains an exocyclic double bond and is a major component of gum spirits of turpentine was of special interest. It was found that β-pinene readily reacted with carbon tetrachloride in the presence of as little as 1 mole per cent. of catalyst (benzoyl peroxide or acetyl peroxide) to give substantially quantitative yields of a one-to-one addition product. However, the addition did not take place normally at the two ends of the double bond in β-pinene. Instead, the addition product (adduct) was still unsaturated possessing one double bond per molecule. Obviously, therefore, isomerization must have occurred and the bicyclic β-pinene must have produced a monocyclic addition product. The adduct was shown

to be 7-trichloromethyl-8-chloro-Δ^1-p-menthene. It is believed that this is the first time that this type of peroxide-catalyzed addition (in which the two fragments add at non-adjacent carbon atoms) has been observed. The chain reaction mechanism shown in Fig. 1 would account quite simply for this structure.

Proof of Structure of the Adduct.—The basis for the assignment of the structure 7-trichloromethyl-8-chloro-Δ^1-p-menthene to the adduct will be apparent from consideration of Fig. 2 and the following evidence. The adduct (I) is optically active and the products of hydrolysis are optically active. The adduct decolorizes alkaline permanganate but gives a negative nitroso chloride test for the $>C{=}C<$ grouping. Quantitative catalytic hydrogenation results in the addition of 1.0 mole of hydrogen per mole of adduct to form the optically inactive (II) 7-trichloromethyl-8-chloro-p-menthane. Hydrolysis of the adduct with concentrated alcoholic alkali produces the optically active acid (III), 7-carboxy-1,8(9)-p-menthadiene. Heating the acid (III) with palladium-carbon at 310–320° produces p-cymene (IV) but dehydrogenation with palla-
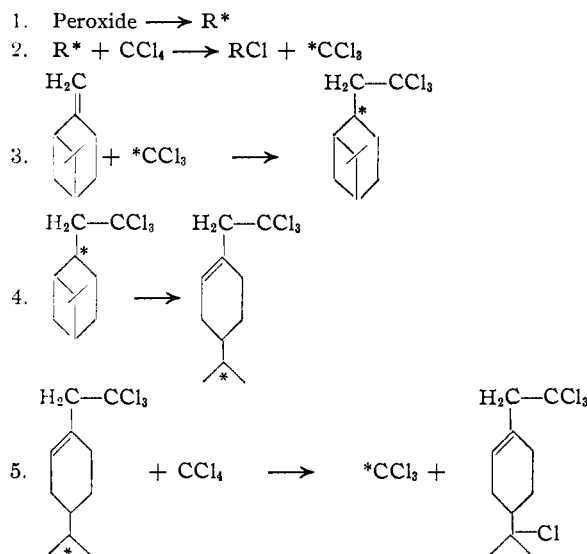

Fig. 1.—Proposed chain reaction for production of 7-trichloromethyl-8-chloro-p-menthene.

(1) Presented in part at the 115th Meeting of the American Chemical Society, San Francisco, California, 1949, before the Division of Organic Chemistry.

(2) M. S. Kharasch, E. V. Jensen and W. H. Urry, *Science*, **102**, 128 (1945); THIS JOURNAL, **67**, 1864 (1945); **68**, 154 (1946); **69**, 1100 (1947); Kharasch, Urry and Jensen, *ibid.*, **67**, 1626 (1945).
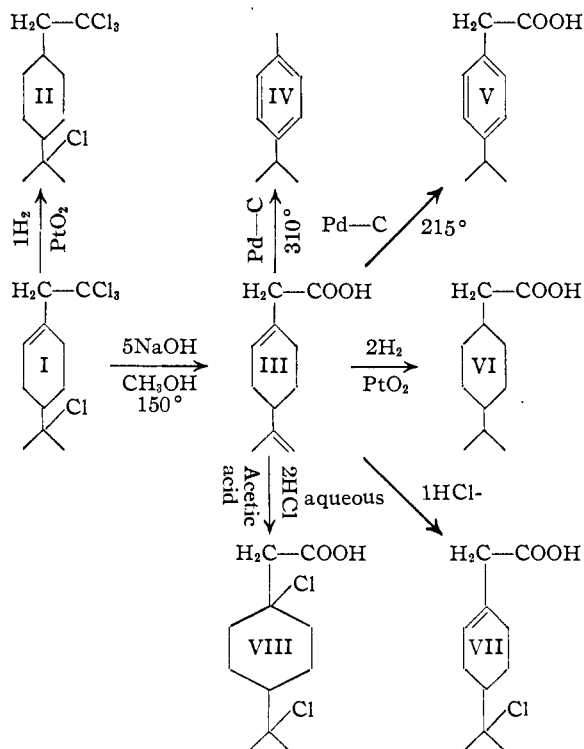

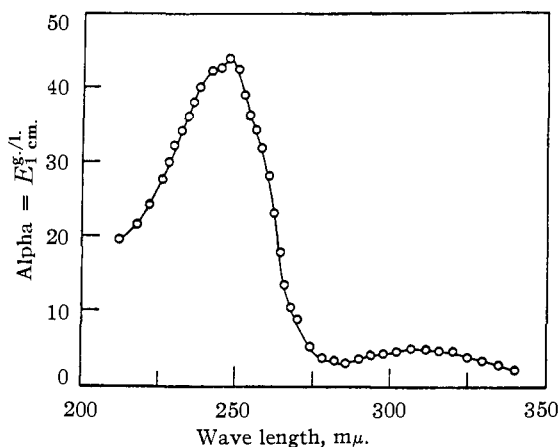Fig. 2.—Reactions of 7-trichloromethyl-8-chloro-p-menthene.

Fig. 3.—Ultraviolet absorption after treatment of adduct with silver nitrate and then with one equivalent of 0.5 N alcoholic alkali.

dium–carbon at 215° produces 7-carboxy-p-cymene (V). The acid (III) absorbs 2.0 moles of hydrogen to form the optically inactive, saturated, 7-carboxy-p-menthane (VI). Also, it forms a monohydrochloride (VII) and the known dihydrochloride (VIII). This establishes conclusively the presence of a p-menthane nucleus in the adduct. Ozonolysis of the acid (III) produces formaldehyde in good yield but formaldehyde could not be detected among the products of ozonolysis of the adduct (I). Nor could acetone, trichloroacetic acid nor chloral be found among the decomposition products obtained after ozonolysis of the adduct. On the other hand, a water-insoluble, non-distillable product was isolated in 87% yield from the decomposed product of ozonolysis of the adduct. The ozonolysis data as well as the loss of optical activity on hydrogenation indicate that the double bond of the adduct is in the ring. One-fourth of the chlorine in the adduct (I) is readily and quantitatively removed by alcoholic silver nitrate at room temperature. Quantitative catalytic hydrogenation of this product shows the presence of two double bonds but the ultraviolet absorption spectrum shows the absence of conjugated unsaturation. Further, one-fourth of the chlorine in the hydrogenated adduct (II) is also readily removed by alcoholic silver nitrate at room temperature. This establishes the presence of an isolated chlorine atom attached to a tertiary carbon atom of the adduct. Ozonolysis of the products obtained by treatment with alcoholic silver nitrate results in the formation of both formaldehyde and acetone. The isolated chlorine atom must there-

fore be attached to C-8. The fact that treatment of the adduct with alcoholic silver nitrate does not produce conjugation even though acetone and formaldehyde are obtained after ozonolysis precludes the 2,3 and 3,4 positions for the cyclic double bond and places it in the 1,2 position. Furthermore, treatment of either the adduct (I), or the adduct from which hydrogen chloride has been removed with silver nitrate, with one equivalent of dilute alcoholic alkali produces conjugation as evidenced by the ultraviolet absorption spectrum, Fig. 3. The trichloromethyl group must therefore be attached to a carbon atom adjacent to the double bond in the adduct and this could only come about if the double bond in the adduct were in position 1(2).

Experimental

β-Pinene.—β-pinene was obtained by fractional distillation of gum spirits of turpentine through Podbielniak type columns of approximately 100 theoretical plates. That used typically had the following constants: b. p. 59° at 20 mm., d^{20}_4 0.8665, α^{25}D −18.5° (10-cm. tube). It was estimated to be better than 99% pure β-pinene.

Preparation of 7-Trichloromethyl-8-chloro-Δ'-p-menthene (I).—Typically, a mixture of 681 g. of β-pinene (5 moles), 2308 g. of C. P. carbon tetrachloride (15 moles), and 13 g. of commercial benzoyl peroxide (0.05 mole) was refluxed for five hours in a three-neck, 3-liter flask fitted
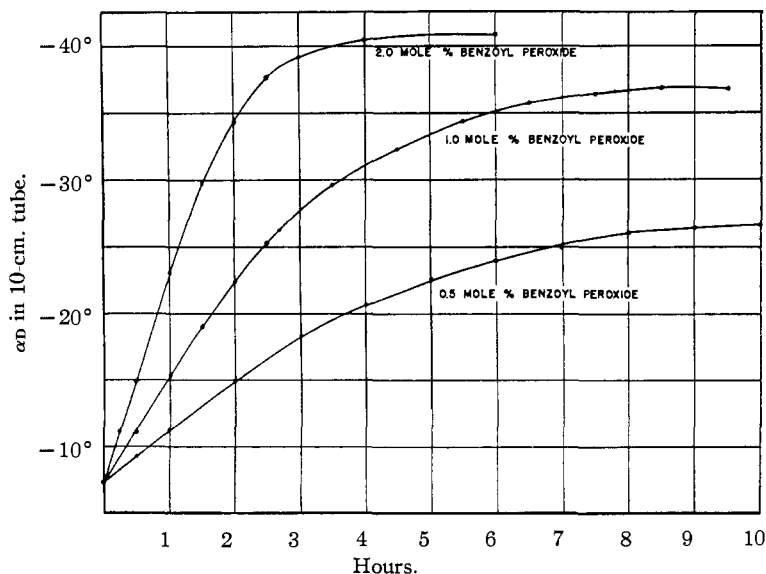

Fig. 4.—Reaction of β-pinene and carbon tetrachloride.

with a reflux condenser, a thermometer and a sampling tube. Since the adduct is optically active, the progress of the reaction may readily be followed by observation of the optical activity of the reaction mixture, Fig. 4. During refluxing the temperature gradually rose to 90° and the rotation dropped to −37° (10-cm. tube). Effluent gases were led through barium hydroxide solution (or alternatively into a soda lime tube) to absorb any carbon dioxide evolved. Typically, only 0.36 g. of carbon dioxide (0.008 mole) was trapped and a few drops of moisture were observed to have formed during the reaction. After the refluxing was completed the reaction product was steam-distilled until the distillate contained less than 1 ml. of oil per 10 ml. of distillate. The optical activity of the oil in the distillate indicated the presence of unreacted

β-pinene and 86 g. of β-pinene was recovered from it by fractional distillation. Titration of an aliquot of the combined aqueous layers from the steam distillation showed the presence of only 0.02 equivalent of acid. The dry residue obtained (crude adduct) weighed 1225 g. which represents a yield of about 85% on the basis of the β-pinene used or 97% on the basis of the β-pinene used and not recovered. When 2 mole per cent. of benzoyl peroxide was used as a catalyst the dry residue obtained after three hours of refluxing weighed about 1400 g., representing a yield of about 97% on the basis of the β-pinene used. The crude product is already fairly pure, solidifying at 40.2–43.8°; but it can conveniently be purified further by crystallization from about five times its weight of alcohol. The most highly purified adduct obtained after successive recrystallization from ethyl alcohol, acetone, and methanol melts at 46–46.5°. Its specific rotation (ca. 10% in alcohol) is −61.8°.

Anal. Calcd. for $C_{11}H_{16}Cl_4$: C, 45.54; H, 5.56; Cl, 48.90; mol. wt., 290.1. Found: C, 45.64; H, 5.74; Cl, 48.49; mol. wt., 294 (cryoscopic in benzene).

Acetyl peroxide or peroxidized turpentine may be used instead of benzoyl peroxide and even simple illumination with ultraviolet light will promote the addition reaction.

7-Trichloromethyl-8-chloro-*p*-menthane (II).—The adduct (1.000 g.) was dissolved in 10 ml. of glacial acetic acid and hydrogenated in the presence of 25 mg. of Adams platinum oxide catalyst in a quantitative catalytic hydrogenator similar to that described by Joshel.[3] Hydrogen in an amount corresponding to 1.04 double bonds per $C_{11}H_{16}Cl_4$ molecule was absorbed. The hydrogenated adduct was recovered by filtering off the catalyst and diluting with water. When recrystallized from methanol the hydrogenated adduct melted at 74.5–75.5°. Larger quantities of the same product readily could be obtained by catalytic hydrogenation in a Parr hydrogenation apparatus (15 g. adduct, 50 ml. acetic acid, and 100 mg. platinum oxide).

7-Carboxy-1,8(9)-*p*-menthadiene (III).—The adduct is not readily nor appreciably hydrolyzed by aqueous alkali even when heated to 140° under pressure. However, it is readily hydrolyzed by alcoholic alkali and different products are obtained under different conditions. For the preparation of 7-carboxy-1,8(9)-*p*-menthadiene (III), a mixture of 184 g. of the adduct (0.65 mole), 510 ml. of methanol and 144 g. of sodium hydroxide (3.6 moles) dissolved in 170 ml. of water was heated for six hours at 150° in an oscillating autoclave. The reaction product was then diluted with 500 ml. of water, distilled to remove methanol, and the alkaline residue extracted with ether to remove neutral material. The alkaline solution was then acidified with hydrochloric acid and again extracted with ether. Evaporation of the ether left 59 g. of crude acid. When this was distilled there was obtained 31.3 g. of acids boiling at 121–131° at 0.4 mm. which were solid at room temperature. Repeated recrystallization from pentane raised the melting point to 34–35°. The crystalline acid is optically active [α]D −43.6° (ca. 10% in alcohol). When hydrogenated catalytically it absorbs hydrogen in an amount corresponding to 2.0 double bonds per molecule but examination of the ultraviolet absorption spectrum indicates that the two double bonds are not conjugated. Also, the acid readily absorbs 2 moles of bromine, showing that it is not α,β-unsaturated.

Anal. Calcd. for $C_{10}H_{15}COOH$: C, 73.31; H, 8.95; neutral equivalent, 180.2. Found: C, 73.19; H, 8.87; neutral equivalent, 180.3.

7-Carboxy-*p*-menthane (VI).—The crystalline acid (III) (0.5 g.) when dissolved in 10 ml. of glacial acetic acid and hydrogenated in the presence of 25 mg. of Adams platinum oxide catalyst absorbed hydrogen in an amount corresponding to 2.00 double bonds. The 7-carboxy-*p*-menthane was recovered by filtering off the catalyst and diluting with water. After three crystallizations from pentane it melted at 81–83°. Larger quantities of the

same product could be obtained readily by catalytic hydrogenation in a Parr hydrogenation apparatus. The acid was not optically active.

Anal. Calcd. for $C_{10}H_{19}COOH$: C, 71.68; H, 10.94; neutral equivalent, 184.3. Found: C, 71.50; H, 10.90; neutral equivalent, 184.3.

8-Chloro-7-carboxy-1-*p*-menthene (VII).—This compound was prepared simply by mixing together the crystalline acid (2 g.) and aqueous concentrated hydrochloric acid (5 ml.) and shaking for a short while. After allowing to stand overnight, the semisolid, oily layer (2.5 g.) was separated off and taken up in heptane. On cooling there was obtained 1.7 g. of a crystalline solid melting at 67–74°. Two additional crystallizations from pentane raised the melting point to 81–81.5°. The monohydrochloride is optically active [α]D −66.6° (ca. 3% in heptane). When hydrogenated in the presence of Adams platinum oxide catalyst it absorbed hydrogen (with slight evolution of hydrogen chloride) in an amount corresponding to 1.1 mole of hydrogen per mole of $C_{11}H_{17}O_2Cl$. The chlorine could be determined quantitatively by treatment with alcoholic silver nitrate.

Anal. Calcd. for $C_{11}H_{17}O_2Cl$: Cl, 16.36. Found: Cl, 16.28, 16.44.

1,8-Dichloro-7-carboxy-*p*-menthane (VIII).—One gram of 7-carboxy-1,8(9)-*p*-methadiene was dissolved in 10 ml. of glacial acetic acid saturated with hydrogen chloride gas. Ten ml. of concentrated aqueous hydrochloric acid was then added, the mixture allowed to stand in a refrigerator overnight, and the crystalline precipitate which formed filtered off. After two recrystallizations from heptane there was obtained 0.8 g. of a product melting at 150–152° (sealed capillary). Bain[4] reported that 1,8-dichloro-7-*p*-menthanecarboxylic acid melts at 153° and admixture with an authentic sample of his acid did not depress the melting point.

Dehydrogenation and Decarboxylation of 7-Carboxy-1,8(9)-*p*-menthadiene (III).—Ten grams of the acid, 7-carboxy-1,8(9)-*p*-menthadiene, was mixed with 10 g. of palladium–carbon (5% palladium) and heated at 310–320° for five hours. The product was leached with ether and the ethereal solution washed with alkali to remove acids. The ether was evaporated and the residue was distilled. There was obtained 7 g. of oil n^{20}D 1.4909 boiling at 175°. The ultraviolet absorption spectrum of this product was substantially identical with that of an authentic sample of *p*-cymene (n^{20}D 1.4909; b. p. 175°). Oxidation with dilute nitric (1:4) gave *p*-toluic acid m. p. 178–182° which did not depress the melting point of an authentic sample of *p*-toluic acid.

Another portion of the acid (7 g.) was mixed with 300 mg. of palladium–carbon and heated to 215°. The mixture was stirred vigorously and held at this temperature for two hours. After cooling, 30 ml. of heptane was added to the mixture, the catalyst removed by filtration, and successive crystalline fractions were obtained by stepwise cooling of the solution. Two fractions melting at 48–50° were thus obtained in addition to 2.5 g. melting at or above room temperature. The material melting at 48–50° did not depress the melting point of an authentic sample of 7-carboxy-*p*-cymene prepared by the chloromethylation of cumene, conversion to the nitrile and hydrolysis of the nitrile essentially according to a standard method.[5] In addition, the ultraviolet absorption spectrum of the acid obtained on dehydrogenation of 7-carboxy-1,8(9)-*p*-menthadiene was substantially identical with that of the authentic 7-carboxy-*p*-cymene, Fig. 5.

Dehydrochlorination with Silver Nitrate.—One-fourth of the chlorine present in the adduct (I) and the dihydroadduct (II) could be removed readily and quantitatively by treatment with alcoholic silver nitrate at room temperature. Typically, 0.2 mole was dissolved in 500 ml. of methanol and to this was added a solution of 0.21 mole of silver nitrate dissolved in 500 ml. of aqueous methanol

(3) L. M. Joshel, *Ind. Eng. Chem., Anal. Ed.*, **15**, 590 (1943).

(4) J. P. Bain, THIS JOURNAL, **68**, 638 (1946).
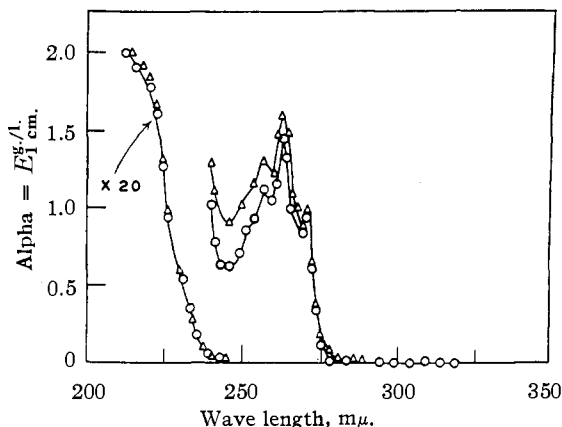
(5) "Organic Syntheses," Coll. Vol. I, p. 437.

Fig. 5.—Comparison of ultraviolet absorption spectra of V and authentic 7-carboxy-*p*-cymene: O, synthetic; △, from adduct.

(80%). After standing for several hours the precipitated silver chloride was filtered off and the filtrate diluted with water. The light yellow oil which separated was drawn off, washed, dried, and weighed. Recovery of silver chloride and of dehydrochlorinated product was substantially quantitative (0.2 mole of each). The oil obtained from the adduct typically had the constants: n^{20}D 1.5149 and αD (10-cm. tube) $-64.1°$. The oil obtained from the dihydro adduct had n^{20}D 1.5019 and was optically inactive. The products thus obtained on dehydrochlorination of the dihydro adduct and of the adduct when subjected to quantitative catalytic hydrogenation absorbed hydrogen in an amount corresponding to approximately 1 and 2 double bonds per molecule, respectively. Ultraviolet absorption spectra indicated that the two double bonds in the product obtained by dehydrochlorination of the adduct are not conjugated. Portions of each preparation were distilled and several portions taken in the distillation range 65–83° at 0.01 to 0.04 mm. Ozonolysis of selected fractions indicated the presence of both terminal methylene and isopropylidene groupings in both products.

Dehydrochlorination with Dilute Alcoholic Alkali.—To a solution of 2.0 g. of the adduct (I) dissolved in 180 ml. absolute alcohol was added 20 ml. of 1.01 N aqueous alkali, and the mixture was refluxed. Aliquots were removed from time to time and ultraviolet absorption spectra of the solutions were taken and the amount of unreacted alkali remaining was determined by titration with acid. At the end of fifteen minutes titration indicated that 0.59 mole of chloride per mole of adduct had been removed and the presence of considerable conjugation was indicated by a characteristic maximum in the absorption curve at 248 mμ. Calculations based on the presence of 10.0 g. of absorbing material per liter of the aliquot indicated an extinction coefficient $E_{1cm.}^{1\%}$, 27.7. At the end of one hour, 1.68 equivalents of chlorine had been removed and the extinction coefficient was 35.4; at the end of two hours 2.10 equivalents of chlorine had been removed and the extinction coefficient was 50.0. Refluxing for an additional two hours resulted in the removal of additional chlorine but did not significantly affect the ultraviolet absorption.

By reason of the relatively low value of the extinction coefficient of the product obtained when only 0.59 equivalent of chlorine was removed it could not be stated with certainty that removal of a single chlorine atom from the adduct produces conjugation. Apparently the alcoholic alkali attacked both the isolated tertiary chlorine at C-8 and one of the chlorine atoms of the trichloromethyl group simultaneously. To settle this point some of the adduct from which the tertiary chlorine had been removed with alcoholic silver nitrate was treated with alcoholic alkali.

The adduct, 1.45 g. was refluxed with 12.5 ml. of 0.40 N alcoholic alkali (slightly less than 1 equivalent) for one hour. By then 0.85 equivalent of chlorine had been removed. The ultraviolet absorption curve of this solution indicated a very high degree of conjugation, showing a maximum at 247.5 mμ (Fig. 3), thus indicating that removal of a single chlorine from the trichloromethyl group produces conjugation.

Ozonolysis by the method of Doeuvre[6] was used to determine terminal methylene groups semiquantitatively. No formaldehyde was obtained from the adduct. On a molar basis, β-pinene, which contains one terminal methylene group and the acid (III) yielded equal amounts of formaldehyde, and the products of dehydrochlorination with silver nitrate yielded about half as much.

Semiquantitative estimation of isopropylidene groups was obtained by ozonolysis according to the method of Kuhn and Roth.[7] No acetone was obtained from either the adduct or the acid (III), but about half as much on a molar basis was obtained from the products of dehydrochlorination with silver nitrate as was obtained from neoabietic acid,[8] which contains one isopropylidene group.

A solution of 14.5 g. (0.05 mole) of adduct (I) in 200 ml. of pentane was ozonized at 0°. The theoretical amount of ozone, 2.4 g. (0.05 mole), was absorbed. The ozonide was decomposed by refluxing with water for four hours. During the reflux period the solvent and any volatile products were carried to a Dry Ice trap by a slow stream of nitrogen. No significant amount of acetone, formaldehyde, or other products could be detected in the trap. The decomposition product was separated into water-soluble and ether-soluble portions in the usual manner. The only detectable water-soluble product was 3.1 g. (0.085 mole) of hydrogen chloride. The ether-soluble product remaining after removal of the solvent was an orange-brown oil weighing 11.5 g. Attempts to distill this product at 0.2 mm. pressure led to extensive loss of hydrogen chloride, but no distillate. The ether-soluble, water-insoluble product plus the hydrogen chloride in the aqueous phase accounts for 87% of the ozonide.

Summary

Preparation of 7-trichloromethyl-8-chloro-Δ^1-*p*-menthene by the peroxide-catalyzed addition of carbon tetrachloride to β-pinene is described.

The reactions used to determine the assigned structure are presented in detail.

A free radical chain mechanism is proposed to explain the formation of this adduct.

In determining the structure of the adduct other new compounds were prepared. These include 7-trichloromethyl-8-chloro-*p*-methane, 7-carboxy-1,8(9)-*p*-menthadiene and 7-carboxy-*p*-menthane.

NEW ORLEANS, LA.   RECEIVED OCTOBER 20, 1949

(6) J. Doeuvre, *Bull. soc. chim.*, [5] **3**, 612–620 (1936).

(7) R. Kuhn and H. Roth, *Ber.*, **65**, 1285–1292 (1932).

(8) G. C. Harris and T. F. Sanderson, THIS JOURNAL, **70**, 334 (1948).